Germanium Saturated with Gallium Antimonide

J. O. McCaldin
Hughes Semiconductors, Newport Beach, California

AND

D. B. Wittry
University of Southern California, Los Angeles, California

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Single crystals of Ge saturated with GaSb were prepared by temperature gradient zone melting at 750°C. Electron probe microanalysis indicated 4.83×10^{20} Ga atoms and 2.36×10^{20} Sb atoms/cc in the saturated material with an estimated error of about 10%. Thus the solubility of Sb is greatly enhanced by the presence of Ga, though the reverse is not true. Hall measurements were in semiquantitative agreement with the chemical concentration measurements and indicated that carrier mobility is not much affected by the presence of the compensating impurity.

I. INTRODUCTION

UNTIL recently, the doping concentrations commonly employed in semiconductors such as germanium have generally been low enough so that the semiconducting medium could be regarded as a dilute solution. However, the heavily doped materials which are now finding applications in tunnel diodes, parametric diodes, and transistors can no longer be regarded as dilute solutions.[1,2] Quantitative measurements of non-dilute behavior are needed, e.g., measurement of dopant solubilities in the germanium-rich corner of a ternary system. Such measurements for the Ge-Ga-Sb system are reported in this work.

One may ask, first of all, whether a quasi-binary system, Ge vs GaSb, exists within the Ge-Ga-Sb ternary system. Conditions for the existence of a quasi-binary are well known,[3] and the known terminal binary phase diagrams[4] for this ternary system strongly suggest that the quasi-binary will occur. Metallographic sections of alloys of Ge and GaSb have shown two phases to be present in a eutecticlike structure.[5] Furthermore, thermal analysis[5] of the alloys indicated the evolution of a large latent heat at 648°±4°C. Thus, the available evidence supports the existence of a quasi-binary system, Ge vs GaSb, of the eutectic type. However, there is evidence that this quasi-binary system is not "ideal" in the sense that the terminal phases do not have zero solubility for the other components. If the system were ideal, the quasi-binary would lie along the line called "complete compensation" in Fig. 1. Instead, the Ge-rich phase has been found to be p type in all cases examined.[5] Thus, the actual quasi-binary must include compositions to the Ga-rich side of "complete compensation."

It is also known that the solubilities in this system, although small for ordinary metallographic work, are not zero. Heretofore only solubilities in the two binary systems GeGa and GeSb have been determined.[6] For dilute solutions it is usually assumed that the solidus in the ternary system can be deduced by superposition of the separate solubilities in the appropriate binary systems. This would lead to a parallelogram-shaped solidus enclosing the shaded area in Fig. 1. However, other experiments[1,2] indicate qualitatively that interaction effects are likely to lead to enhanced solubilities in the ternary system.

The present paper will deal with the experimental determination of a point on the solidus of the ternary phase diagram and some properties of an alloy of this composition.

II. ATTAINMENT OF EQUILIBRIUM

An important consideration in solubility determinations is the attainment of equilibrium between the solid solution being studied and the liquid phase from which it is formed. This is paramount in semiconductor solid solutions where, as one investigator has remarked, ". . . over the years there has been a pronounced tendency for the 'accepted' equilibrium solid solubilities to decrease. . . ." [6] In particular, for the quasi-binary system Ge vs GaSb, it has been found that very rapid solidification will produce a metastable solid solution,[7] suppressing completely the eutectic character which the alloys exhibit at equilibrium.

Exploratory measurements for the present study were made on specimens prepared by the "regrowth" or "alloy fusion" process. These specimens were formed by solid-liquid interfaces moving at average speeds somewhat less than 10^{-4} cm/sec, which would commonly be considered a slow growth rate in crystal pulling technology.[8] Nevertheless, the composition of the solid

[1] J. O. McCaldin, J. Appl. Phys. **31**, 89 (1960).
[2] D. B. Wittry, J. M. Axelrod, and J. O. McCaldin, *Properties of Elemental and Compound Semiconductors* (Interscience Publishers, Inc., New York, 1959), p. 89.
[3] F. N. Rhines, *Phase Diagrams in Metallurgy* (McGraw-Hill Book Company, Inc., New York, 1956), Chap. 17.
[4] M. Hansen and K. Anderko, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958).
[5] J. O. McCaldin, Bull. Am. Phys. Soc. Ser. II, **5**, 105 (1960).
[6] F. A. Trumbore, Bell System Tech. J. **39**, 205 (1960).
[7] P. Duwez, R. H. Willens, and W. Klement, Jr., J. Appl. Phys. **31**, 1500 (1960).
[8] M. Tanenbaum in *Semiconductors*, edited by N. B. Hannay (Reinhold Publishing Corporation, New York, 1959), p. 107.

was found to be sensitive to fluctuations in the rate of solidification. Figure 2 shows a typical regrowth with the relevant microchemical analysis obtained by the electron probe x-ray microanalyzer.[2] This regrowth was formed by placing a 0.030-in. thick slice of GaSb on a 0.080-in. thick slice of Ge. The assembly was heated in argon to 800°C and then cooled by reducing the temperature of the furnace containing the specimen 20°C every five minutes. The steps produced in the specimen solidification rate correspond to lines visible in the photomicrograph of Fig. 2. In a number of cases, these lines can in turn be correlated with the changes in both the Ga and Sb concentrations.

Because of the concentration fluctuations in the regrown specimens, it was decided to analyze a Ga-saturated Ge specimen prepared by temperature gradient zone melting[9] (TGZM) for comparison with an earlier solubility determination[2] on a specimen prepared by the regrowth method. The TGZM method gave average interface speeds of 5×10^{-7} cm/sec or less, and also resulted in nearly constant temperature for the growth of the entire specimen. A chemical analysis by the microanalyzer showed that the Ga concentration in the TGZM specimen was reduced some 27% from that in the regrowth specimen. As a result, further measurements in this study were all made on specimens prepared by TGZM.

III. PREPARATION OF SPECIMENS

In the present adaptation of the TGZM technique, a slice of the desired solute, e.g., GaSb, about 0.015 in. thick was placed between two slices of Ge, each about 0.080 in. thick. This "sandwich" assembly, with the slices horizontal, was placed in a resistively heated furnace consisting of upper and lower half-shells. Only the upper half-shell was used to heat the slices, thus producing a vertical temperature gradient perpendicular to the slices. A slowly flowing argon atmosphere protected the slices and the temperature at the slices was 750°±5°C. About five days were required for the melt to come through the top surface of the sandwich assembly.

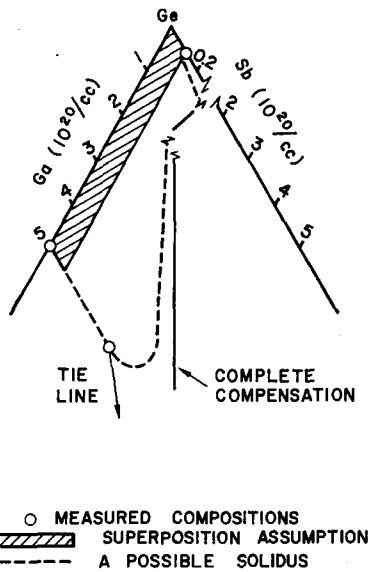

FIG. 1. Solid solution region at the Ge-rich corner of the ternary system GeGaSb at 750°C. The figure compares (1) the solution range expected by assuming superposition of solubilities[6] from the binary systems GeGa and GeSb with (2) a measured solidus composition. The tie line connects this measured solidus composition with a liquid composition in the quasi-binary system Ge-GaSb.

Specimens of Ge saturated with Ga and with GaSb were prepared. Alternate metallographic examination and polishing was used to locate single-crystal regions suitable for the cutting of specimens for Hall measurements. Several sizes and shapes of Hall specimens were prepared; however, the five specimens studied most intensively were large specimens having six arms, each similar to that sketched in the work cited in footnote 10. Each of these specimens was subjected successively to Hall measurement, chemical analysis by the electron probe x-ray microanalyzer,[2] and spectrographic chemical analysis.

IV. MEASUREMENT OF CONCENTRATIONS

Two types of concentration measurements were made. First, the chemical concentrations of gallium and antimony were measured by microanalyzer and spectrographic techniques. Secondly, the concentrations of free carriers were obtained by Hall measurements.

The microanalyzer measurements of Ga and Sb are shown in Table I. The table reports measurements made at 28 randomly chosen locations in one of the Ga-saturated specimens, and at 13 randomly chosen locations in one of the GaSb-saturated specimens. The average number of Geiger counts obtained are shown for each specimen, together with the rms deviation in counts for the various locations measured. Since the rms deviation is observed to be approximately the square root of the number of counts, we may conclude that the principal error in these measurements comes from the counting statistics. Proceeding in the usual way to calculate probable errors for the microanalysis, one finds that the standard errors (rms deviation of the mean) in the intensity ratio K of Ga and Sb, with respect to a GaSb standard, are about 1% and 5%, respectively. However, an error of 10% is estimated for the calculated conversion of K values to atomic concentrations (see Appendix). Thus the rather low statistical error that was obtained in measuring Ga concentrations is overridden by uncertainties in standardization.

Spectrographic measurements of concentration were made on ten specimens using synthetic standards. The concentrations obtained in this way scattered relatively widely between specimens as well as between different

[9] W. G. Pfann, *Zone Melting* (John Wiley & Sons, Inc., New York, 1958).

[10] T. H. Geballe in *Semiconductors*, edited by N. B. Hannay (Reinhold Publishing Corporation, New York, 1959), p. 346.

TABLE I. Microanalyzer measurements of gallium and antimony concentrations in germanium.

Specimen	Ga in Ge[b]	GaSb in Ge	
Element	Ga	Ga	Sb
Signal			
Average counts	2535	2610	390
rms deviation	60.7	66.4	30.6
No. measurements	28	13	13
Standard error (cts.)	11.5	18.4	8.5
Background			
Average counts	1030	1075	190
rms deviation	27.2	36.6	20.2
No. measurements	10	7	8
Standard error (cts.)	8.5	13.8	7.2
GaSb standard			
Average counts	46 486	47 416	17 908
Concentration			
K value	0.0324	0.0324	0.0112
Standard error	0.9%	1.5%	4.7%
Standardization factor[a]	0.329	0.329	0.465
Estimated error	---------- 10% or Less ----------		----------
Atomic concentration	1.065%	1.065%	0.521%
	4.83×10^{20}	4.83×10^{20}	2.36×10^{20}
Estimated total error	10.0%	10.1%	11.1%

[a] See Appendix.
[b] All data in the first column was obtained on a different day from the remaining data.

parts of a single specimen. In view of the greater consistency obtained by the microanalyzer method, we will not treat the spectrographic results further. An average of all the spectrographic readings is given in Table II, however.

Hall measurements were made on three of the GaSb-saturated specimens and on two of the Ga-saturated specimens. A field of 5000 gauss was used, and the specimens carried a current I_x of 1 amp. The specimens were immersed in an isothermal oil bath at 298°K. The resulting Hall voltage V_y fell in the range of 5 to 10 μv and had to be read against a typical I_xR voltage drop between specimen arms of some 100 μv. In order to gain some idea of the errors in these measurements, each of the five specimens studied was measured several times. The resulting values of Hall concentration N_H and Hall mobility μ_H were plotted on log-log paper as shown in Fig. 3; for each specimen, the plotted values lie on a straight line of slope $=-1$, as would be expected if the experimental error in the parameter V_y dominates. Inspection of Fig. 3 indicates that the variation from specimen to specimen is no greater than the uncertainty in the measurement of an individual specimen, thus suggesting that no systematic error in specimen preparation is more important than the uncertainty in the Hall voltage V_y.

The Hall measurements allow one to distinguish between Ga-saturated and GaSb-saturated specimens. The average values of N_H for each type of specimen are given in Table II.

V. DISCUSSION

The ternary composition which has been studied can be compared to well-known alloys in the relevant binary systems, GeGa and GeSb. The available data permits us to compare solubilities as well as carrier mobilities.

The concentrations of Ga and Sb in the studied composition are given most accurately by the microanalyzer measurements. They indicate that the concentration of Ga present in the Ga-rich solidus compositions is about 1%, independently of whether Sb is present or not. A markedly different behavior occurs, however, on the Sb-rich side of the studied composition, where the Sb concentration is enhanced about twenty-fold over its value[6] in the GeSb binary. These results appear plausible in terms of the Fermi level expected in these materials and the effect of the Fermi level on the ionization of the dopants. An estimate of the effect of Fermi levels on solubility can be made assuming that, (1) since the minority impurity atoms are almost all ionized, the concentration of the ionized atoms fixes the minority impurity solubility, and (2) the concentration of ionized minority impurity atoms can be deduced from Boltzmann statistics together with

TABLE II. Comparison of concentrations measured by various methods.

	Ga in Ge	GaSb in Ge		
Method	[Ga]	[Ga]	[Sb]	[Sb]/[Ga]
Microanalyzer	4.83×10^{20}	4.83×10^{20}	2.36×10^{20}	49.2%
Estimated error	10.0%	10.1%	11.1%	···
Spectrographic	···	5.97×10^{20}	3.07×10^{20}	51.4%
Estimated error	···	~30%	~30%	···
		$p=[\text{Ga}]-[\text{Sb}]$		
Hall measurements	8.19×10^{20}	4.92×10^{20}		40%[b]
Trumbore[a]	4.9×10^{20}			

[a] Work cited in footnote 6.
[b] Assuming that the concentration of Ga is the same in the compensated and the uncompensated material.

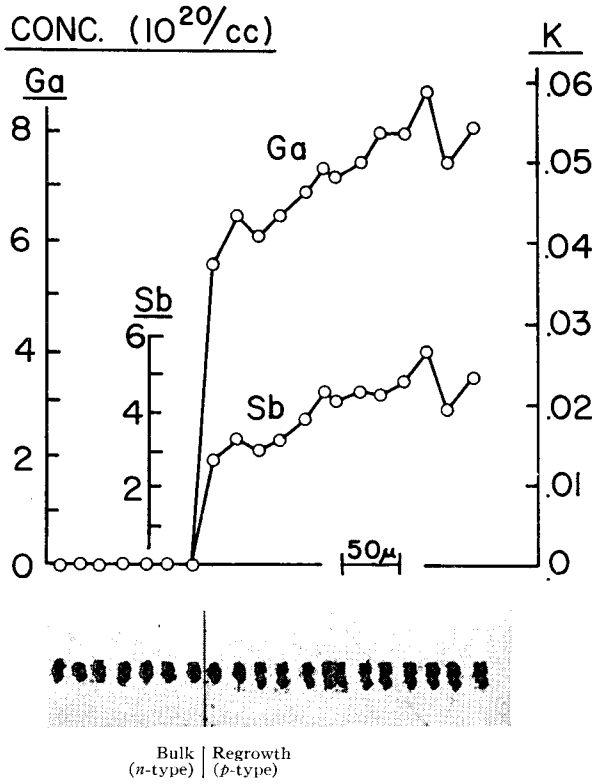

FIG. 2. Photomicrograph of GaSb regrowth in Ge. The row of contamination spots indicates locations at which Ga and Sb concentrations were measured with the microanalyzer. The Ga concentrations were measured in sequence; the stage was then displaced (10 μ) and a parallel scan made for the Sb concentration. The specimen was etched with CP-4 after analysis.

Blakemore's calculation[11] for the shift in Fermi level, E_F, with concentration. The plot given by Blakemore[11] indicates that the Fermi level is about the same in the studied composition and in Ge saturated with Ga, but some $3.3kT$ higher for Ge saturated with Sb. The usual analysis[12] would indicate that a change of $3.3kT$ in Fermi level would cause a change in the concentration of ionized Sb atoms by a Boltzmann factor of $e^{3.3}=27.1$. The agreement with the observed enhancement of Sb solubility is quite good in view of the approximations[11–13] involved and experimental errors.

The Hall measurements made on these materials are in approximate agreement with the chemical concentration measurements just discussed. However, the Hall concentrations are larger than the corresponding chemical concentrations by more than expected experimental error, as indicated in Table II. Trumbore made a similar observation[14] but doubted that the effect was real owing to the large experimental errors, which he estimates may be as high as $\pm 50\%$ or more. In the present study we cannot rule out the possibility of systematic errors of this size, in view of the relatively small Hall voltage measured. Thus the absolute Hall concentrations are presumed subject to large errors compared to the microanalyzer concentrations. In regard to relative concentrations, however, the Hall measurements are in better agreement with the chemical measurements, as indicated by the Sb/Ga ratio in Table II.

The Hall mobility measurements shown in Fig. 3 are subject to the same criticism. Systematic errors may be present in the mobility values; however, comparisons of mobility between the two types of specimens treated in the figure can be made. This is true because the present data indicate the reproducibility of repeated measurements on a given specimen, as well as the variation between specimens nominally of the same composition. Examination of Fig. 3 indicates that, within experimental error, the mobility is the same whether Ge is saturated with Ga or with GaSb.

VI. CONCLUSIONS

Germanium saturated with GaSb at 750°C contains 4.83×10^{20} Ga atoms and 2.36×10^{20} Sb atoms/cc with an experimental error estimated to be about 10%. The solubility of Ga is the same as in the GeGa binary system; however, the solubility of Sb is about twenty-fold larger than in the GeSb binary. The enhanced Sb solubility appears plausible in view of expected Fermi level effects on the ionization of Sb. Hall measurements of these heavily doped materials give concentrations greater than the corresponding chemical concentrations by somewhat more than the expected experimental error and the Hall mobility is unaffected, within experimental error, by the presence of the compensating impurity.

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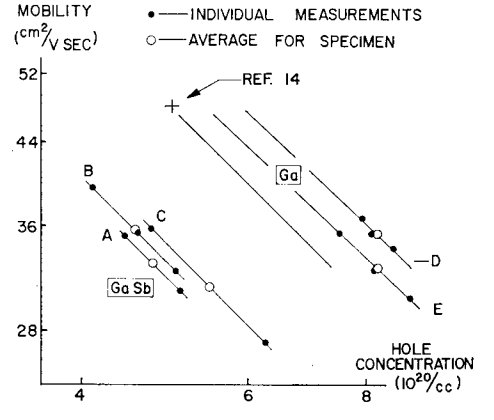

FIG. 3. Plot of Hall measurements for TGZM specimens. Three specimens (A, B, and C) are Ge saturated with GaSb and two specimens (D and E) are Ge saturated with Ga. The referenced[14] point is for Ga-doped Ge.

[11] J. S. Blakemore, Proc. Phys. Soc. (London) **71**, 692 (1958).
[12] C. S. Fuller in *Semiconductors*, edited by N. B. Hannay (Reinhold Publishing Corporation, New York, 1959), Chap. 6.
[13] H. Brooks, J. Phys. Chem. Solids **8**, 546 (1959).
[14] F. A. Trumbore and A. A. Tartaglia, J. Appl. Phys. **29**, 1511 (1958).

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APPENDIX. STANDARDIZATION OF THE MICROANALYSIS

The intensities of the Ga $K\alpha$ radiation and the Sb $L\alpha$ radiation obtained in analysis of the TGZM specimens were standardized by referring these intensities to the intensities of the same x-ray lines obtained from a specimen of GaSb. In each case, the ratio of the intensity from specimen to that from standard is designated by the parameter K, and it is necessary to find a relationship between the "K" values and atomic concentration. This was done by assuming (1) that the *primary* intensity which is produced in the specimen is directly proportional to mass concentration, and (2) that the observed intensity differs from the intensity produced only because of self-absorption. The first assumption is valid provided the elements in the target are not widely separated in atomic number so that the retardation of the electrons is nearly independent of composition. In this connection, it should be noted that the x-ray intensities were measured for fixed charge collected by the target, a method which in some cases provides a partial compensation for the differences due to different atomic number.[15] The second assumption neglects the fluorescence excitation which may occur as a result of the absorption of the continuum in the specimen or the absorption of characteristic radiation. The fluorescence excitation by the continuum amounts to a few percent of the direct excitation and is a serious source of error only in special cases.[16,17] The fluorescence excitation by the characteristic radiation is important if strong emission lines occur close to and on the short-wavelength side of the absorption edge of the observed x-ray line. Since this is not true for either the standard or the two TGZM specimens, fluorescence excitation by characteristic radiation was also neglected.

If K^* represents the ratio of the true intensities from unknown and from standard, then

$$K_A^*=\frac{X_A}{X_A+(1-X_A)(M_B/M_A)}\times\frac{X_A'+(1-X_A')}{X_A'}(M_B'/M_A'),$$

where M_A and M_B are the atomic weights of element A and B (g/mole) in the unknown, M_A' and M_B' are the atomic weights of elements A' and B' in the standard, X_A and X_A' are the atomic concentration of element A in the unknown and standard, respectively. If $X_A \ll 1$ we may neglect X_A and X_AM_B/M_A with respect to M_B/M_A. Also, since $M_A=M_A'$ and for $X_A'=0.5$, we have

$$K^*=X_A[(M_A'+M_B')/M_B].$$

In both specimens element B is germanium and the standard is GaSb, hence for both Ga in Ge and Sb in Ge,

$$X_A=0.379K^*.$$

The value of K is related to K^* by the self-absorption correction. The self-absorption correction was obtained from the correction curve of Castaing and Descamps[16] (the correction for differing instrument geometry was negligible), using the mass absorption coefficients given in Table III. In cases where tabulated values of the mass absorption coefficients could not be found, the values used were obtained by extrapolation of values for elements of similar atomic number, assuming the mass absorption coefficient to be proportional to $Z^3\lambda^3$.

TABLE III. Mass absorption coefficient used in self-absorption correction.

Absorber	Ge	Ga	Sb	GaSb
Ga $K\alpha$ rad ($\lambda=1.34$ A)	41	41	205	146
Sb $L\alpha$ rad ($\lambda=3.44$ A)	629	~580	448	520

The result of applying the appropriate self-absorption correction to both the radiation from the specimen and from the standard is

$X_A=0.329K$ for Ga in Ge, and

$X_A=0.465K$ for Sb in Ge.

It is interesting to compare the present standardization with previous work in which GaAs was used as a standard for determining the solubility of Ga in Ge.[2] In that case, the principal correction was for fluorescence excitation of the Ga $K\alpha$ line by the $K\alpha$ and $K\beta$ lines of As. The ratio of intensity of Ga $K\alpha$ from GaAs to that from GaSb was observed with the microanalyzer to be 1.59. On this basis, the present standardization agrees with the previous one to within 8%.

Note added in proof. Solubility measurements for GaSb in Ge were reported recently by V. M. Glazov, D. A. Petrov, and S. N. Chizhevskaya, Izvest. Akad. Nauk S.S.S.R., Met. i Topl. **4**, 153 (1959). Using microhardness measurements and microscopy to study quenched alloys, they obtained a solubility of about 1 wt % GaSb in Ge at 750°C. This value appears to be too small in view of the present results, although comparison is complicated by their implicit assumption of an "ideal" quasi-binary.

[15] D. B. Wittry, Ph.D. thesis, California Institute of Technology, Pasadena, California, 1957.

[16] R. Castaing and J. Descamps, J. phys. radium **16**, 304 (1955).

[17] D. B. Wittry, "Metallurgical applications of electron probe microanalysis," *Eighth Annual Conference on Applications of X-Ray Analysis, Denver, Colorado, 1959* (Plenum Press, New York, to be published).